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PATENT APPLICATION TRANSMITTAL LETTER

Attorney's Docket No. 00-2-025

TO THE COMMISSIONER OF PATENTS AND TRADEMARKS:

Transmitted herewith for filing is the patent application of: Raj P. Singh and Robert G. Mendenhall

for HETEROGENITE MATERIAL FOR MAKING SUBMICRON COBALT METAL POWDERS

Enclosed are:

- ☒ Patent specification including 2 sheet(s) of drawing
- ☒ An assignment of the invention to OSRAM SYLVANIA Inc.
- ☒ Declaration and Power of Attorney
- ☐ Associate Power of Attorney

Claims As Filed				
For	Number Filed	Number Extra	Rate	Fee
Total Claims	5	0	\$18.00	\$ 0.00
Independent Claims	2	0	\$78.00	\$ 0.00
Basic Fee				\$ 690.00
Total Filing Fee				\$690.00

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August 31, 2000

Date

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00-2-025

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Singh et al.

Serial No.: Herewith

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For: HETEROGENITE MATERIAL FOR MAKING SUBMICRON COBALT METAL POWDERS

Hon. Commissioner of Patents and Trademarks
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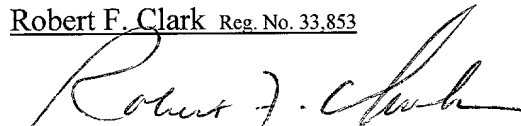
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PATENT APPLICATION
EXPRESS MAIL NO. EL128140385US
ATTORNEY'S DOCKET NO. 00-2-025
COVER SHEET

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

TITLE: Heterogenite Material for Making Submicron Cobalt Powders

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Heterogenite Material for Making Submicron Cobalt Powders

5 TECHNICAL FIELD

This invention relates to cobalt compounds and methods of making cobalt powders. In particular, this invention relates to HCoO_2 (heterogenite) and methods for making submicron cobalt powders.

10 BACKGROUND ART

Submicron particle size ($<1 \mu\text{m}$) cobalt powders exhibit distinct advantageous properties over larger, micron size ($>1 \mu\text{m}$) powders. For example, in tungsten carbide applications, submicron size cobalt particles greatly improve sinterability and mass transport at temperatures significantly below the sintering temperatures required for micron-size cobalt powders. Typically, submicron cobalt metal powder is made via thermal decomposition of cobalt oxalate (CoC_2O_4). However, this method is not very efficient as CoC_2O_4 contains only 40 wt.% Co compared to 53.6 wt.% Co in $\text{Co}(\text{OH})_3$. Hence, it would be advantageous to use a compound having a higher cobalt content such as cobalt hydroxide to make submicron cobalt powders.

U.S. Patent No. 4,218,240 teaches the conversion of $\text{Co}(\text{OH})_3$ to a micron-size cobalt metal powder having a FSSS value of 1.3 - 1.4 μm . Impure CoCl_2 in solution is converted to $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ which is then converted to $\text{Co}(\text{OH})_3$ by decomposition with NaOH . Cobalt powder is produced by direct reduction of the wet cobalt hydroxide in hydrogen at 300-500°C. Although the patent describes air drying of the $\text{Co}(\text{OH})_3$ at 100°C to form a hydrated cobaltic oxide, it also teaches that air drying is not necessary

prior to reducing the cobalt containing precipitate. No sub-micron powders are described.

SUMMARY OF THE INVENTION

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It is an object of the invention to obviate the disadvantages of the prior art.

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It is another object of the invention to provide a high-cobalt-content precursor material for making submicron cobalt metal powders.

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In accordance with the objects of this invention, there is provided a heterogenite powder having a surface area of at least about 90 m²/g.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a TG-DTA curve of a room-temperature-dried Co(OH)₃ precipitate.

Fig. 2 is an SEM photomicrograph of the heterogenite powder of this invention.

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Fig. 3 is an SEM photomicrograph of the submicron cobalt powder made from the heterogenite powder of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims taken in conjunction with the above-described drawings.

It was discovered that a high surface area HCoO_2 (heterogenite) material could be made by drying a wet cobalt hydroxide precipitate at a moderate temperature of 110°C . The surface area as measured by the conventional BET method was at least about 90 m^2/g and preferably about 90 m^2/g to about 110 m^2/g . The high surface area HCoO_2 is then be reduced under a hydrogen-containing atmosphere to form submicron-size cobalt metal powders.

Preferably, the HCoO_2 is reduced at a temperature from about 325°C to about 425°C for about 0.5 hours to about 2.0 hours. The particle size of the resultant cobalt metal powders ranges from 0.4 to 0.9 μm as determined by Fisher Sub-Sieve Sizer (FSSS). The HCoO_2 contains about 64 wt.% Co.

A wet cobalt hydroxide precipitate may be made by decomposing $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ with NaOH as described in U.S. Patent No. 4,218,240. The wet cobalt hydroxide, $\text{Co}(\text{OH})_3$, which contains about 30-32 weight percent (wt.%) Co, may be represented by the chemical formula $\text{Co}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$. After drying at room temperature, it converts to a compound which may be represented as $\text{HCoO}_2 \cdot x\text{H}_2\text{O}$ where $0 < x < 1$. The room-temperature-dried $\text{Co}(\text{OH})_3$ precipitate is a layered compound wherein water molecules reside between layers of HCoO_2 . After heating at 110°C , the room-temperature-dried $\text{Co}(\text{OH})_3$ precipitate loses all of its water molecules and converts to HCoO_2 . This change is illustrated in Fig. 1 which is a TG-DTA curve of a room-temperature-dried $\text{Co}(\text{OH})_3$ precipitate. The water loss from the room-temperature-dried $\text{Co}(\text{OH})_3$ precipitate is marked by an endothermic peak in the differential thermal analysis (DTA) curve at about 110°C . Upon further heating to greater than above 150°C , the HCoO_2 converts to cobalt oxide, Co_3O_4 .

The following non-limiting examples are presented.

EXAMPLE 1

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Wet cobalt hydroxide was dried at various temperatures: ambient temperature (24-25 °C), 110 °C and 316 °C. These temperatures were selected on the basis of a differential thermal analysis (DTA) of $\text{Co}(\text{OH})_3$. HCoO_2 was obtained after heating wet $\text{Co}(\text{OH})_3$ at 110°C. The presence of HCoO_2 was confirmed by x-ray diffraction (XRD). The compound contained about 62 - 63.2 wt.% cobalt and possessed a high surface area of 90-110 m^2/g (BET method). Scanning electron micrographs of HCoO_2 powders (e.g., Fig. 2) demonstrated that it contained aggregates of very fine particles.

EXAMPLE 2

The HCoO_2 powder made in Example 1 was placed into two graphite boats, which were placed in a tube furnace. The samples were reduced at 400°C in hydrogen (10 SCFH flow rate) using a 4°C/min temperature gradient and 2 hour reduction time. The resulting cobalt metal powder was characterized by SEM and other methods. The cobalt powder was submicron size having a FSSS of 0.87 μm . This is significantly lower than 1.3-1.4 μm size of cobalt particles produced according to the method in U.S. Patent No. 4,218,240. The morphology of the particles is presented in Fig. 3. Powder porosity was 0.812 and the BET surface area was 1.97 m^2/g .

EXAMPLE 3

The HCoO_2 powder made according to Example 1 was reduced as in Example 2 except that no temperature gradient was used. The
5 resultant cobalt powder had a FSSS of 0.78μ , a porosity of 0.825 and a BET surface area of $2.07 \text{ m}^2/\text{g}$.

EXAMPLE 4

10 The HCoO_2 powder made according to Example 1 was reduced at 350°C in hydrogen (10 SCFH flow rate) for 2 hour using a $4^\circ\text{C}/\text{min}$ temperature gradient. The resultant cobalt powder had a FSSS of $0.65 \mu\text{m}$, a porosity of 0.856, and a BET surface area of $2.19 \text{ m}^2/\text{g}$.

EXAMPLES 5-12

The following examples demonstrate the effect of time, temperature and hydrogen flow rate on the size of the cobalt
20 metal powders produced from the high surface area HCoO_2 .

Examples	Time (h)	Temp (°C)	H ₂ -Flow Rate (SCFH)	FSSS (μm)
5	1	375	10	0.55
6	1	375	10	0.64
7	1.5	325	15	0.4
8	0.5	425	15	0.76
9	1.5	425	15	0.94
10	1.5	425	5	0.75
11	0.5	425	5	1.05
12	1	375	10	0.68

While there has been shown and described what are at the present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

CLAIMS

We claim:

1. A heterogenite powder having a surface area at of least about 90 m²/g.
2. The heterogenite powder of claim 1 wherein the surface area is from about 90 m²/g to about 110 m²/g.
3. A method for making a submicron particle size cobalt powder comprising reducing a heterogenite powder having a surface area at least about 90 m²/g.
4. The method of claim 3 wherein the heterogenite powder has a surface area from about 90 m²/g to about 110 m²/g.
5. The method of claim 3 wherein reducing the heterogenite powder comprises heating the heterogenite powder in a hydrogen-containing atmosphere at a temperature from about 325°C to about 425°C for about 0.5 hours to about 2.0 hours.

ABSTRACT

A high-surface-area heterogenite (HCoO_2) material is described
5 for use in making submicron cobalt metal powders. The HCoO_2
material has a surface area of at least about $90 \text{ m}^2/\text{g}$ and is
preferably produced by dehydrating a cobalt hydroxide
precipitate at 110°C .

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FIG. 1 is a graph showing the DTA and TG curves of a sample. The DTA curve shows a broad endothermic peak around 100°C and a sharp endothermic peak around 250°C. The TG curve shows a corresponding weight loss starting around 100°C and reaching a plateau around 250°C.

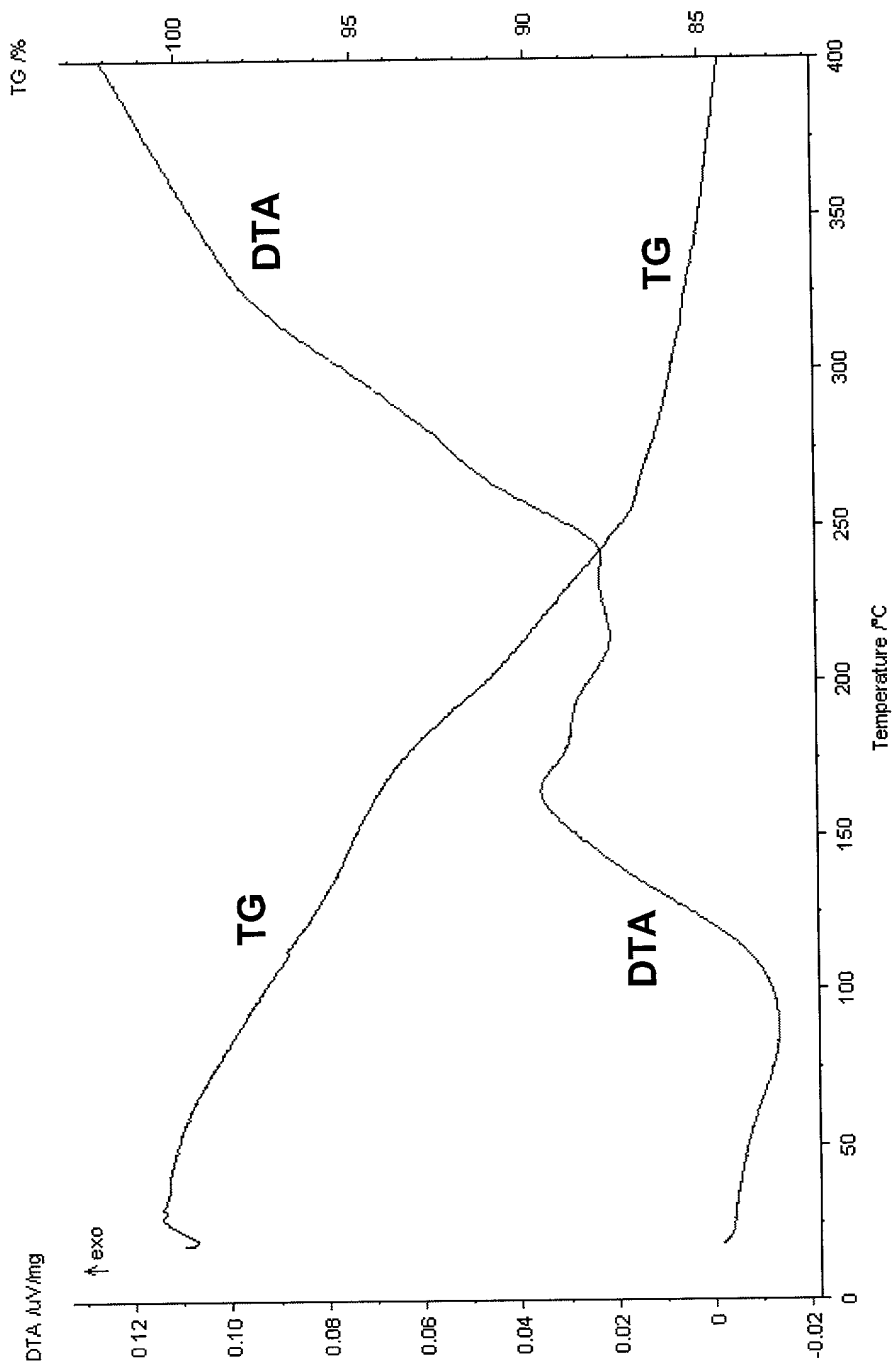


FIG. 1

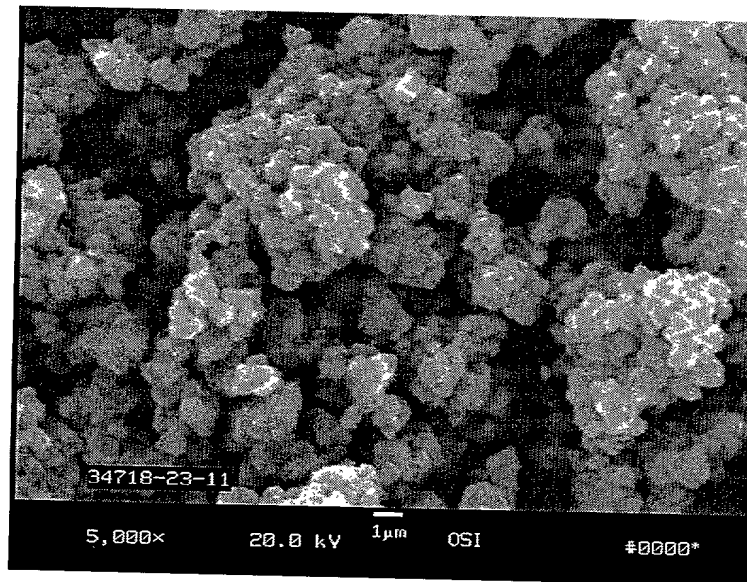


Fig. 2

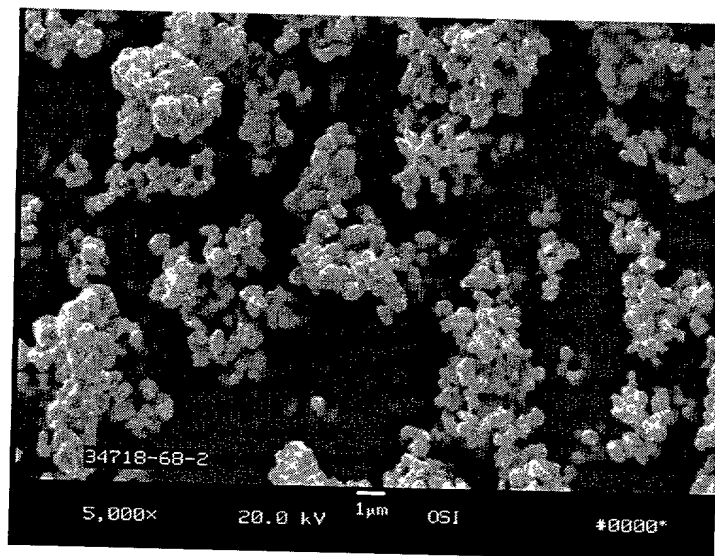


Fig. 3

DECLARATION

As below-named inventors, we hereby declare that:

Our respective residences and citizenship are as stated below.

We believe we are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled "Heterogenite Material for Making Submicron Cobalt Powders," the specification of which is being filed concurrently herewith, identified as attorney docket no. 00-2-025.


We hereby state that we have reviewed and understand the contents of the above-identified specification including the claims, as amended by any amendment specifically referred to in this declaration.

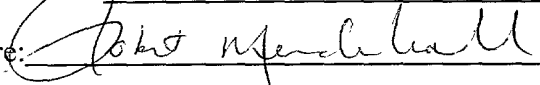
We acknowledge the duty to disclose all information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56 .

We hereby appoint Robert F. Clark, Reg. No. 33,853 to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Please send all correspondence to:

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We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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